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THE STRUCTURE OF THE SPECTRA OF DOUBLY AND TREBLY IONIZED ZIRCONIUM

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ABSTRACT

The spectra emitted by Zr atoms which are doubly and trebly ionized have been observed with the grating and prism spectrographs of the National Bureau of Standards and with the vacuum grating spectrograph of the University of Alberta. These spectra have been analyzed and the series relationships involved in them have been established. The terms which have been found to account for the spectra are without exception those required by the quantum theory. Zr IV is a doublet spectrum which results from the migration of a single electron which, in its unexcited state, occupies a 4_3 orbit. From a series of S terms an ionization potential of 33.83 v is derived, corresponding to a value of 274,067 cm^{-1} for the lowest term $4^2D_{\frac{3}{2}}$. Zr III consists of singlet and triplet systems, the terms of which result from the interaction of two electrons occupying 4_3 orbits in their unexcited state. Sequences of ^1D and ^3D terms have been found which result when one of the electrons occupies an n_1 orbit, the other remaining in a 4_3 orbit. These term sequences place the ground term, $^3F_2$, at 194,441 cm^{-1}, which gives 24.00 v as the ionization potential of Zr^{++}. Among the Zr III multiplets are those representing the transition $4f \rightarrow 4d$. These multiplets and also those representing intersystem combinations exhibit anomalous intensities.

CONTENTS

I. INTRODUCTION

The spectra emitted by zirconium electrodes in air, when arc or condensed spark discharges pass between them, have been recognized as emanating from the Zr atom in its neutral and successively ionized stages. Lists of wave lengths of these spectra, covering the range from 9,300 A in the infra-red to 2,160 A in the ultra-violet, were published a few years ago by one of us (C. C. K.).[2] The successful classification of nearly all the stronger lines of these lists into multiplet structures characteristic of Zr I, Zr II, Zr III, and Zr IV revealed the fact that some of the more prominent features of the spectra of doubly and trebly ionized Zr were to be sought for in the Schumann region and beyond. For theoretical reasons, it was obvious that these unknown spectra should contain more lines than were reported by Bowen and Millikan [3] and by McDonald, Sutton, and McLay.[4] Therefore, we planned a new survey of the ultra-violet portions of the spectrum, the region down to 2,000 A to be observed with the Hilger E$_1$ quartz prism spectrograph at the National Bureau of Standards, the remainder with the vacuum grating spectrograph at the University of Alberta, Edmonton, Canada.

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[2] B. S. Sci. Papers, No. 548, 22, p. 47; 1927.
[3] Phys. Rev., 28, p. 924; 1926.
[4] Trans. Royal Soc. (Canada) (III), 20, p. 313; 1926.

II. EXPERIMENTAL PROCEDURE

The electrodes used in this investigation, for both the Bureau of Standards and the University of Alberta observations, were cut from the same rod of zirconium metal kindly supplied to us for spectrographic analysis by Dr. H. C. Rentschler, of the Westinghouse Research Laboratory. It is a pleasure to acknowledge here our indebtedness to him for supplying us with this material, which proved to be of high purity, although containing traces of Fe, Ni, Ti, Al, Sn, Cb, and Si.

For the Bureau of Standards observations, the light sources were either arc or spark discharges maintained between the Zr electrodes. The arcs were operated on 240 volts d. c., at current strengths of 4 or 5 amperes. The spark discharges were supplied by a transformer which stepped-up 110 volts a. c. to 40,000 volts. A condenser of 0.006 μf capacity was connected in parallel across the high-voltage terminals of the transformer. Exposures to the spark were usually juxtaposed to arc exposures, and these in turn to exposures to the Fe or Cu arcs which furnished the comparison spectra.

By setting the prism carriage of the E_1 spectrograph forward 5 cm from the original position, it was possible to photograph the spectrum down to wave length 1,920 A with the aid of Schumann plates. Owing to the lack of reliable standards below 2,000 A no great accuracy is claimed for the Zr wave lengths measured in this region on the Bureau of Standards spectrograms. Above 2,000 A, however, the standards of reference were chosen from both the Fe and Cu arc spectra, for which the wave lengths determined by Burns and Walters [5] and by Mitra,[6] respectively, were used in the reductions. To Doctor Burns we are indebted for a copy of the new Fe standards in advance of publication.

The University of Alberta observations were made with the vacuum spectrograph which has been adequately described elsewhere.[7] Two gratings, each of 2 m radius, were used in this spectrograph to obtain the Zr spectra. For the region 2,100 to 630 A the grating ruled with 30,000 lines per inch and giving a dispersion of 4.5 A per millimeter was employed. The other grating, dispersion 8.5 A per millimeter, was used to photograph the extreme ultra-violet portion between 720 and 280 A. The source, a spark discharge between the Zr terminals supplied by a large X-ray coil, with suitable capacity and an external spark gap in parallel, was operated both in a vacuum and in an atmosphere of hydrogen. The observations in hydrogen, which extend down to 1,470 A, the limit of transparency of the fluorite window which separated the source from the vacuum chamber of the spectrograph, served the very excellent purpose of separating the lines according to the degree of ionization of the radiating atom. Strong lines observed in the hydrogen source but not in the vacuum source were due to Zr^+. Lines stronger in hydrogen than in vacuum were due to Zr^{++}, and those stronger in vacuum than in hydrogen were due to the trebly ionized atom. The spectrum as obtained with the vacuum spectrograph is shown in Figure 1.

[5] Pub. Allegheny Observatory, **6**, p. 159; 1929.
[6] Annales de Physique, **19**, p. 315; 1923.
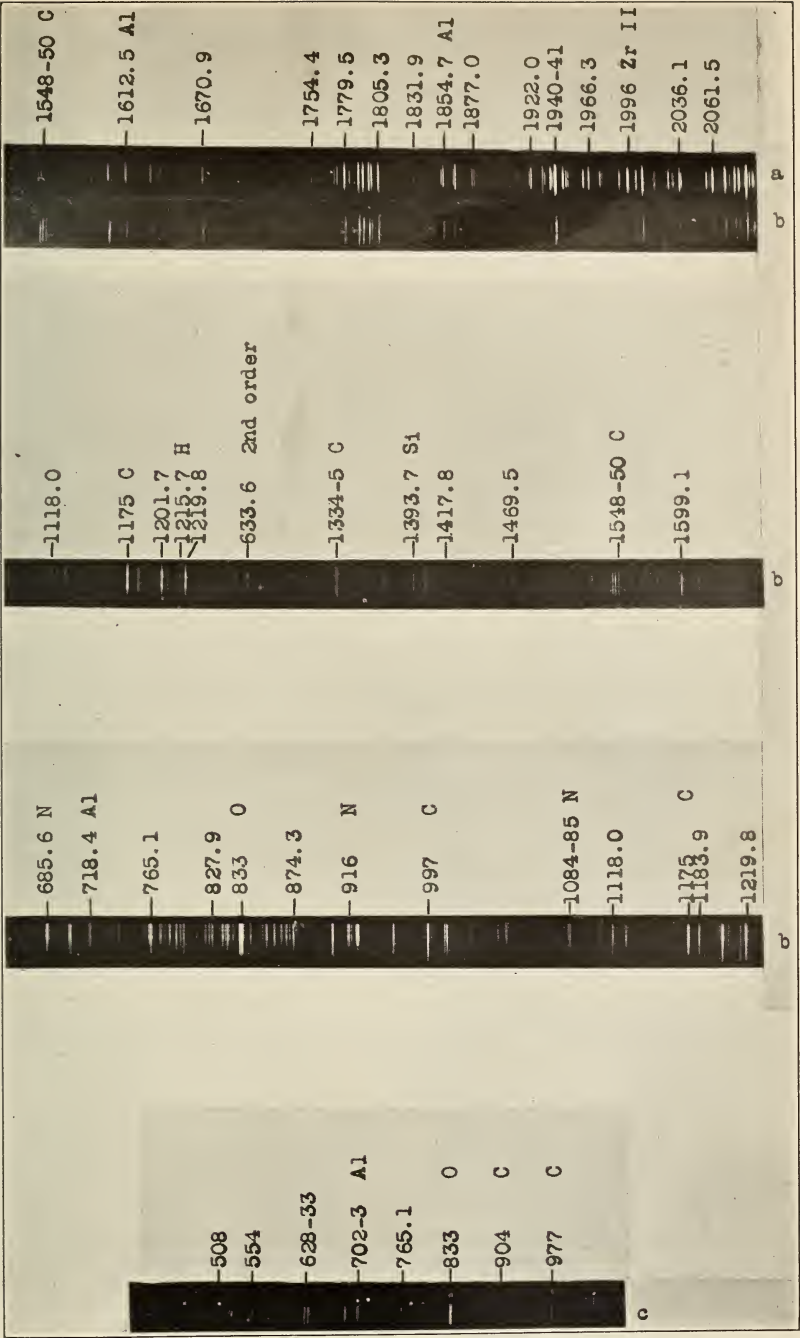[7] J. Opt. Soc. Am., **12**, p. 523; 1926.

FIGURE 1.—*Vacuum-spark spectrum of zirconium*

III. THE SPECTRUM OF TREBLY IONIZED ZIRCONIUM (Zr IV)

In its normal state the Zr atom has four electrons external to the krypton configuration, two bound in 5_1 "orbits" and two in 4_3 "orbits." The trebly ionized atom has lost all but one of these electrons, namely, one of the 4_3 type, which corresponds to a normal energy state designated by the term ^2D. When the Zr^{+++} ion absorbs energy the lone 4_3 electron is dislodged to any one of the unoccupied orbits in the N, O, and P shells, permitted by the rules governing the transition. The energy states assumed by the atom in this process are designated by the term symbols 5^2S, 5^2P, 4^2F, etc. From their work on the stripped atoms of the second long period, Bowen and Milliken [8] were able to designate for Zr IV not only the normal 4^2D state and the excited 5^2P and 4^2F states which combine with it, but also the states 5^2S and 6^2S which combine with 5^2P. A short-time previously Gibbs and White [9] had already detected the 5S-5P doublet by applying the regular doublet law to the 1-valence-electron systems of the periods beginning with Rb and Cs.

To the Zr IV lines thus classified by these earlier investigators we have been able to add a few more. Table 1 contains a list of Zr IV lines which have been definitely established to date, the wave lengths being those derived from the Bureau of Standards and University of Alberta measurements. The

FIGURE 2.—*Term diagram of Zr IV*

terms which account for these lines are given in Table 2, the relative values beginning with 0 for the lowest being entered in the second column. The absolute terms and the Rydberg denominators given in the third and fourth columns result from the series formula

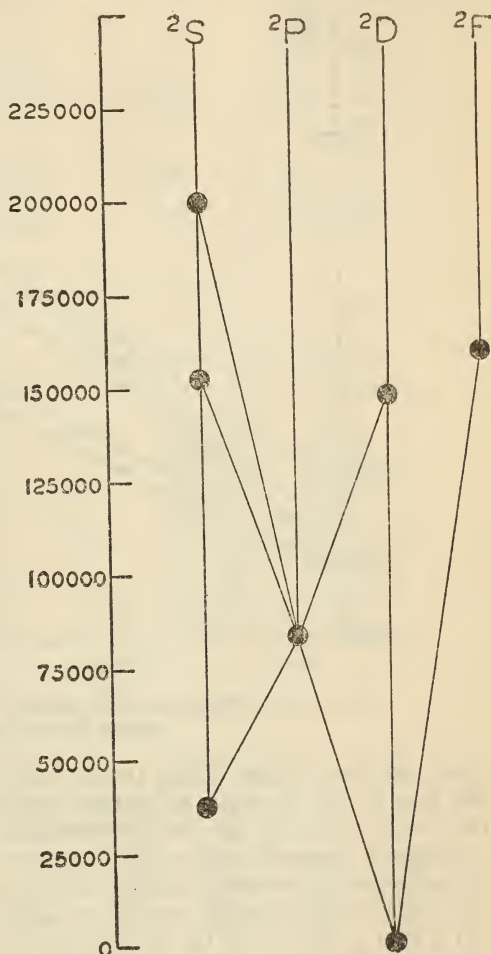$$mS = 16R/\{m - 2.1237 - 6.1556 \times 10^{-7} \ (mS)\}^2$$

[8] Phys. Rev. **23**, p. 924; 1926.   [9] Proc. Nat. Acad. Sci., **12**, p. 551; 1926.

which has been found to satisfy the terms 5S, 6S, and 7S. We therefore find a value 274,067 cm^{-1} for the ground term $4^2D_{\frac{3}{2}}$ of Zr IV, which gives an ionization potential of 33.83 volts for Zr^{+++}. The relative positions of the Zr IV terms are shown graphically in Figure 2.

The successful application, by various investigators, of the irregular doublet law to corresponding terms arising from the same electron configuration in iso-electronic systems has not only afforded a
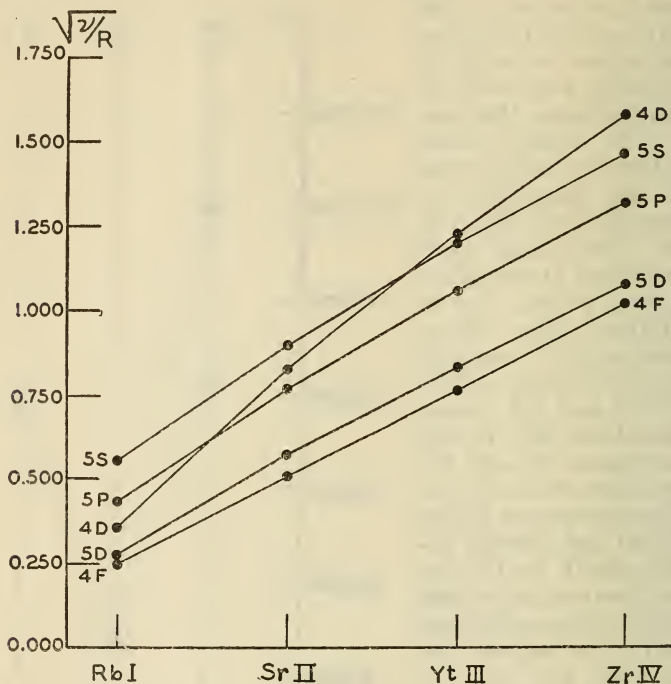

FIGURE 3.—*Values of $\sqrt{\nu/R}$ for the 1 electron systems of the second long period*

check on the identity of the terms, but has established the validity of the law in the domain of optical spectra. According to this law, the values of $\sqrt{\nu/R}$ for the corresponding terms should increase by a constant amount with atomic number. Here ν represents the distance between any term and its limit and R is the Rydberg number. In Table 3 are given the values of $\sqrt{\nu/R}$ for the 4D, 4F, 5S, 5P, and 5D terms of Rb I, Sr II, Yt III and Zr IV. Figure 3 shows these values graphically, whence it is seen that although the curves for the terms with total quantum number 5 are sensibly parallel as the law requires, yet that for 4D deviates markedly from parallelism with the curve for 4F. This effect is already apparent in the similar curves based on the data of Russell and Lang [10] for the 4D and 4F terms of K I, Ca II, Sc III, and Ti IV.

[10] Astrophys. J., **66**, p. 13; 1927,

TABLE 1.—*Classified lines of Zr IV*

λ I. A.	Int.	ν	Δν	Term combination
2, 286. 66	15	43, 718. 39	2, 485. 89	$5^2S_{1/2}-5^2P_{1/2}$
2, 163. 62	15	46, 204. 28		$5^2S_{1/2}-5^2P_{3/2}$
1, 608. 02	4	62, 188	351	$5^2P_{3/2}-5^2D_{3/2}$
1, 599. 00	30	62, 539	2, 486	$5^2P_{3/2}-5^2D_{5/2}$
1, 546. 21	20	64, 674		$5^2P_{1/2}-5^2D_{3/2}$
1, 469. 55	15	68, 048	2, 484	$5^2P_{3/2}-6^2S_{1/2}$
1, 417. 78	5	70, 532		$5^2P_{1/2}-6^2S_{1/2}$
1, 219. 85	45	81, 977	2, 483	$4^2D_{3/2}-5^2P_{1/2}$
1, 201. 76	50	83, 211	1, 249	$4^2D_{5/2}-5^2P_{3/2}$
1, 183. 98	25	84, 460		$4^2D_{3/2}-5^2P_{3/2}$
874. 29	10	114, 378	2, 486	$5^2P_{3/2}-7^2S_{1/2}$
855. 69	4	116, 864		$5^2P_{1/2}-7^2S_{1/2}$
633. 56	30	157, 838	1, 230	$4^2D_{5/2}-4^2F_{7/2}$
628. 66	20	159, 068		$4^2D_{3/2}-4^2F_{5/2}$

TABLE 2.—*Terms of Zr IV*

Term type	Relative value	Δν	Absolute value	Rydberg denominator
$4^2D_{3/2}$	0	1, 250	274, 067	2. 5311
$4^2D_{5/2}$	1, 250		272, 817	2. 5369
$5^2S_{1/2}$	38, 258		235, 809	2. 7287
$5^2P_{1/2}$	81, 976	2, 486	192, 091	3. 0232
$5^2P_{3/2}$	84, 462		189, 605	3. 0431
$5^2D_{3/2}$	146, 650	351	127, 417	3. 7121
$5^2D_{5/2}$	147, 001		127, 066	3. 7172
$6^2S_{1/2}$	152, 509		121, 558	3. 7976
$4^2F_{5/2}$	159, 068	20	114, 999	3. 9074
$4^2F_{7/2}$	159, 088		114, 979	3. 9077
$7^2S_{1/2}$	198, 840		75, 227	4. 8275

TABLE 3.—*Values of $\sqrt{\nu/R}$ for Rb I, Sr II, Yt III, and Zr IV*

Terms	Rb I	Δ	Sr II	Δ	Yt III	Δ	Zr IV
4D	0. 361	*0. 462*	0. 823	*0. 405*	1. 228	*0. 350*	1. 578
4F	. 251	*. 254*	. 505	*. 258*	. 763	*. 261*	1. 024
5S	. 554	*. 346*	. 900	*. 298*	1. 198	*. 268*	1. 466
5P	. 437	*. 332*	. 769	*. 289*	1. 058	*. 262*	1. 320
5D	. 270	*. 300*	. 570	*. 265*	. 835	*. 242*	1. 077
6S	. 351	*. 262*	. 613	*. 232*	. 845	*. 207*	1. 052

IV. THE SPECTRUM OF DOUBLY IONIZED ZIRCONIUM (Zr III)

A striking feature of the spark spectrum of zirconium in the region extending from 2,900 A to 2,400 A is a group of intense lines which do not appear at all in the arc. Since many of the strong lines of Zr II are readily excited in the arc, it was apparent that these lines are characteristic of a spectrum requiring greater excitation energy than does Zr II. It was soon possible to classify many of them as resulting from combinations of high ³P, ³D, and ³F terms with a

common ³D term. Accordingly, in the list of Zr wave lengths, published a few years ago,[11] they were appropriately designated as belonging to Zr III. The tentative classification of these lines was shortly thereafter communicated to Professors Gibbs and White,[12] of Cornell University, who were able not only to verify them, but also to identify the similar combinations of Cb IV by applying the irregular doublet law to the 2-electron systems of Sr I and Yt II. In their paper they suggest an alternative to the term ³F₄ communicated to them, which the analysis of the spectrum here presented verifies.

The realization that a richer spectrum exists for Zr III than that represented by the lines just described led to the survey of the far ultra-violet with the University of Alberta vacuum spectrograph, as mentioned above. This survey revealed the strong groups of lines in the regions 2,000 to 1,700 Å and 870 to 750 Å which involve the low and metastable states of Zr^{++}.

The spectrum of doubly ionized zirconium results from the interaction of the two 4_3 electrons in their normal and excited states. The terms arising from these electrons when unexcited are ¹S, ¹D, ¹G, ³P, and ³F, of which the latter is most stable. When one of the electrons is removed to an available unoccupied orbit in the N and O shells, new energy states arise, which, according to theory, are represented by the terms of Table 4.

TABLE 4.—*Theoretical terms of Zr III*

Electron configuration	Terms									
$4d \cdot 4d$		¹S,	¹D,	¹G			³P		³F	
$4d \cdot 5s$			¹D,					³D		
$4d \cdot 5p$		¹P°,	¹D°,	¹F°				³P°,	³D°, ³F°	
$4d \cdot 5d$	¹S,	¹P,	¹D,	¹F,	¹G,		³S,	³P,	³D, ³F	³G
$4d \cdot 6s$			¹D						³D	
$4d \cdot 4f$		¹P°,	¹D°,	¹F°,	¹G°,	¹H°		³P°,	³D°, ³F°, ³G°	³H°

All the terms of Table 4, except $5d$¹G and $4f$³H°, have been identified for Zr III. The relative values of these terms are given in Table 5. The triplet system terms were established with little or no difficulty, since most of the important multiplets, as shown in Table 7, have their full quota of lines. The fixing of the singlet terms presented a more difficult problem, since only two of them could be located by means of intersystem combinations. The detection, however, of the triplet multiplets (Table 8) coming from the $4f$ electron furnished the key to the problem. For, the singlet P, D, and F terms, coming from $4f$ and those from $5p$ must combine with the $4d$ singlets to give pairs of lines separated by the $\Delta\nu$'s of the $4d$ singlets. With these pairs of lines located, the only remaining pair of strong lines in the far ultra-violet was regarded as coming from the singlet G° and H° terms. A similar procedure was followed to locate the $5d$ and $6s$ singlet terms. The classification of Zr III lines on the basis of these terms is given in Table 6, in which the term symbols are expressed in the notation recently proposed

[11] B. S., Sci. Papers, No. 548, 22, p. 57; 1927.   [12] Phys. Rev., 31, p. 520; 1928.

as standard by Russell, Shenstone, and Turner.[13] The letter *b* following the intensity estimate of a line indicates that it is nebulous usually a property of lines originating in the high-energy levels of the atom. The letter *d* indicates that the line is double.

TABLE 5.—*Terms of Zr III*

Term No.	Term type	ν	$\Delta\nu$	Electron configuration	Term No.	Term type	ν	$\Delta\nu$	Electron configuration
1	$^3F_2$	0	682.5		32	$^3D_1$	?		
2	$^3F_3$	682.5	804.3		33	$^3D_2$	97,462.0	−31.3	
3	$^3F_4$	1,486.8			34	$^3D_3$	97,430.7		
4	$^1G_4$	2,534			35	$^3P_0$	97,918.2	−5.7	
5	$^1D_2$	3,392		$4d \cdot 4d.$	36	$^3P_1$	97,912.5	784.5	
6	$^1S_0$	3,835			37	$^3P_2$	98,697.0		$4d \cdot 5d.$
7	$^3P_0$	8,061.4	265.4		38	$^3F_2$	103,839.6	632.1	
8	$^3P_1$	8,326.8	513.2		39	$^3F_3$	104,471.7	1,116.6	
9	$^3P_2$	8,840.0			40	$^3F_4$	105,588.3		
10	$^1D_2$	16,122.5			41	$^3G_3$	104,635.8	556.2	
11	$^3D_1$	18,398.6	403.9	$4d \cdot 5s.$	42	$^3G_4$	105,192.0	1,112.4	
12	$^3D_2$	18,802.5	730.7		43	$^3G_5$	106,304.4		
13	$^3D_3$	19,533.2			44	$^1D_2$	107,631.5		
14	$^1D°_2$	53,170.0			45	$^3D_1$	107,309.3	507.7	$4d \cdot 6s.$
15	$^1P°_1$	53,646.7			46	$^3D_2$	107,817.0	496.0	
16	$^1F°_3$	54,071.5			47	$^3D_3$	108,313.0		
17	$^3F°_2$	55,554.9	519.8		48	$^1P°_1$	127,320		
18	$^3F°_3$	56,074.7	1,606.7		49	$^1D°_2$	126,531		
19	$^3F°_4$	57,681.4		$4d \cdot 5p.$	50	$^1F°_3$	131,736		
20	$^3D°_1$	55,613.3	822.2		51	$^1G°_4$	131,406		
21	$^3D°_2$	56,435.5	910.9		52	$^1H°_5$	130,002		
22	$^3D°_3$	57,346.4			53	$^3F°_2$	121,466	−1,940	
23	$^3P°_0$	59,945.6	−248.1		54	$^3F°_3$	119,526	−1,712	
24	$^3P°_1$	59,697.5	658.9		55	$^3F°_4$	117,814		$4d \cdot 4f.$
25	$^3P°_2$	60,356.4			56	$^3G°_3$	122,015	588	
26	$^1S_0$	88,999			57	$^3G°_4$	122,603	400	
27	$^1P_1$	97,879			58	$^3G°_5$	123,003		
28	$^1D_2$	98,058		$4d \cdot 5d.$	59	$^3P°_0$	123,392	202	
29	$^1F_3$	101,413			60	$^3P°_1$	123,594	362	
30	$^1G_4$	?			61	$^3P°_2$	123,956		
31	$^3S_1$	94,767.3			62	$^3D°_1$	131,008	510	
					63	$^3D°_2$	131,518	680	
					64	$^3D°_3$	132,198		

TABLE 6.—*Classified lines of Zr III*

λ I. A.	Intensity and notes	ν	Term combinations
3,021.21	2b	33,089.71	$5d^3P_0 - 4f^3D°_1$
2,984.09	3b	33,501.31	$5d^3P_2 - 4f^3D°_3$
2,974.85	2b	33,605.36	$5d^3P_1 - 4f^3D°_2$
2,870.95	1b	34,821.48	$5p^3P°_0 - 5d^3S_1$
2,869.06	7	34,844.42	$5s^3D_2 - 5p^1P°_1$
2,850.62	3b	35,069.81	$5p^3P°_1 - 5d^3S_1$
2,836.19	10	35,248.22	$5s^3D_1 - 5p^1P°_1$
2,827.90	3	35,351.55	$5p^1P°_1 - 5d^1S_0$
2,775.26	5	36,022.05	$5s^3D_3 - 5p^3F°_2$
2,735.79	20	36,541.72	$5s^3D_3 - 5p^3F°_3$
2,720.08	7	36,752.75	$5s^3D_2 - 5p^3F°_2$
2,715.76	18	36,811.22	$5s^3D_2 - 5p^3D°_1$
2,709.06	18	36,902.25	$5s^3D_3 - 5p^3D°_2$
2,698.31	15	37,049.26	$5s^1D_2 - 5p^1D°_2$
2,696.50	2	37,074.13	$5p^3P°_2 - 5d^3D_3$

[13] Phys. Rev., **33**, p. 900; 1929.

TABLE 6.—*Classified lines of Zr III*—Continued

λ I. A.	Intensity and notes	ν	Term combinations
2, 690. 51	20	37, 156. 66	$5s{}^3D_1-5p{}^3F^\circ_2$
2, 686. 30	20	37, 214. 89	$5s{}^3D_1-5p{}^3D^\circ_1$
2, 682. 18	20	37, 272. 05	$5s{}^3D_2-5p{}^3F^\circ_3$
2, 664. 27	20	37, 522. 59	$5s{}^1D_2-5p{}^1P^\circ_1$
2, 661. 90	3	37, 555. 99	$5p{}^3P^\circ_2-5d{}^3P_1$
2, 656. 48	20	37, 632. 62	$5s{}^3D_2-5p{}^3D^\circ_2$
2, 647. 24	1	37, 763. 96	$5p{}^3P^\circ_1-5d{}^3D_2$
2, 643. 83	20	37, 812. 66	$5s{}^3D_3-5p{}^3D^\circ_3$
2, 634. 33	8	37, 949. 02	$5s{}^1D_2-5p{}^1F^\circ_3$
2, 633. 09	1	37, 966. 89	$5p{}^3P^\circ_0-5d{}^3P_1$
2, 628. 28	20	38, 036. 36	$5s{}^3D_1-5p{}^3D^\circ_2$
2, 620. 57	40	38, 148. 27	$5s{}^3D_3-5p{}^3F^\circ_4$
2, 615. 99	4	38, 215. 05	$5p{}^3P^\circ_1-5d{}^3P_1$
2, 615. 60	4	38, 220. 75	$5p{}^3P^\circ_1-5d{}^3P_0$
2, 608. 73	3b	38, 321. 39	$5d{}^1S_0-4f{}^1P^\circ_1$
2, 607. 42	3b	38, 340. 64	$5p{}^3P^\circ_2-5d{}^3P_2$
2, 593. 68	20	38, 543. 74	$5s{}^3D_2-5p{}^3D^\circ_3$
2, 563. 40	3	38, 999. 01	$5p{}^3P^\circ_1-5d{}^3P_2$
2, 502. 37	1b	39, 950. 07	$5s{}^1D_2-5p{}^3F^\circ_3$
2, 494. 00	5	40, 084. 14	$5p{}^3D^\circ_3-5d{}^3D_3$
2, 492. 08	2	40, 115. 02	$5p{}^3D^\circ_3-5d{}^3D_2$
2, 448. 86	40	40, 822. 96	$5s{}^3D_3-5p{}^3P^\circ_2$
2, 444. 57	25	40, 894. 69	$5s{}^3D_2-5p{}^3P^\circ_1$
2, 438. 65	2d?	40, 993. 85	$5p{}^3D^\circ_2-5d{}^3D_3$
2, 436. 68	1	41, 026. 99	$5p{}^3D^\circ_2-5d{}^3D_2$
2, 420. 62	20	41, 299. 18	$5s{}^3D_1-5p{}^3P^\circ_1$
2, 406. 18	10	41, 547. 00	$5s{}^3D_1-5p{}^3P^\circ_0$
2, 405. 78	12	41, 553. 91	$5s{}^3D_2-5p{}^3P^\circ_2$
2, 382. 60	4	41, 958. 14	$5s{}^3D_1-5p{}^3P^\circ_2$
2, 260. 11	2b	44, 231. 91	$\begin{cases}5s{}^1D_2-5p{}^3P^\circ_2\\5p{}^1P^\circ_1-5d{}^1P_1\end{cases}$
2, 250. 99	3b	44, 411. 09	$5p{}^1P^\circ_1-5d{}^1D_2$
2, 235. 96	1	44, 709. 59	$5p{}^1D^\circ_2-5d{}^1P_1$
2, 227. 05	3b	44, 888. 45	$5p{}^1D^\circ_2-5d{}^1D_2$
2, 203. 58	3b	45, 366. 49	$5p{}^3F^\circ_3-5d{}^1F_3$
2, 178. 46	2b	45, 889. 56	$5p{}^3F^\circ_4-5d{}^1F_3$
2, 139. 86	3	46, 717. 25	$4d{}^3P_2-5p{}^3F^\circ_2$
2, 129. 12	1	46, 952. 87	$5p{}^3F^\circ_4-5d{}^3G_3$
2, 116. 63	4	47, 229. 90	$4d{}^3P_1-5p{}^3F^\circ_2$
2, 116. 32	4	47, 236. 82	$4d{}^3P_2-5p{}^3F^\circ_3$
2, 114. 07	6	47, 287. 08	$4d{}^3P_1-5p{}^3D^\circ_1$
2, 104. 26	1b	47, 507. 51	$5p{}^3F^\circ_4-5d{}^3G_4$
2, 102. 27	10	47, 552. 47	$4d{}^3P_0-5p{}^3D^\circ_1$
2, 100. 28	2	47, 597. 52	$4d{}^3P_2-5p{}^3D^\circ_2$
2, 092. 97	2	47, 763. 75	$5p{}^3F^\circ_3-5d{}^3F_2$
2, 086. 72	25	47, 906. 78	$5p{}^3F^\circ_4-5d{}^3F_4$
2, 077. 83	12	48, 111. 73	$4d{}^3P_1-5p{}^3D^\circ_2$
2, 070. 86	5	48, 273. 64	$5p{}^1D^\circ_2-5d{}^1F_3$
2, 070. 34	12	48, 285. 76	$5p{}^3F^\circ_2-5d{}^3F_2$
2, 065. 60	8	48, 396. 55	$5p{}^3F^\circ_3-5d{}^3F_3$
2, 060. 69	15	48, 511. 84	$4d{}^3P_2-5p{}^3D^\circ_3$

TABLE 6.—*Classified lines of Zr III*—Continued

λ I. A.	Intensity and notes	ν	Term combinations
2, 058. 57	3b	48, 561. 80	$5p^3F^\circ_3-5d^3G_3$
2, 055. 98	8b	48, 622. 97	$5p^3F^\circ_4-5d^3G_5$
2, 043. 61	1	48, 917. 24	$5p^3F^\circ_2-5d^3F_3$
2, 036. 76	4b	49, 081. 74	$5p^3F^\circ_2-5d^3G_3$
2, 035. 26	6b	49, 117. 90	$5p^3F^\circ_3-5d^3G_4$
2, 018. 99	0	49, 513. 66	$5p^3F^\circ_3-5d^3F_4$
2, 008. 17	1b	49, 780. 40	$4d^1D_2-5p^1D^\circ_2$
2, 006. 74	12	49, 815. 87 .	$4d^1S_0-5p^1P^\circ_1$
1, 989. 87	15	50, 254	$4d^1D_2-5p^1P^\circ_1$
1, 975. 00	8	50, 632	$5p^3F^\circ_4-6s^3D_3$
1, 966. 29	20	50, 857	$4d^3P_2-5p^3P^\circ_1$
1, 962. 07	10	50, 966	$5p^3D^\circ_3-6s^3D_3$
1, 946. 66	10	51, 370	$4d^3P_1-5p^3P^\circ_1$
1, 946. 09	4	51, 380	$5p^3D^\circ_2-6s^3D_2$
1, 941. 15	40	51, 515	$4d^3P_2-5p^3P^\circ_2$
1, 940. 32	40	51, 537	$4d^1G_4-5p^1F^\circ_3$
1, 937. 29	15	51, 618	$4d^3P_1-5p^3P^\circ_0$
1, 936. 63	15	51, 636	$4d^3P_0-5p^3P^\circ_1$
1, 934. 35	2	51, 696	$5p^3D^\circ_1-6s^3D_1$
1, 932. 58	4	51, 744	$5p^3F^\circ_3-6s^3D_2$
1, 922. 02	20	52, 028	$4d^3P_1-5p^3P^\circ_2$
1, 914. 07	0	52, 244	$5p^3F^\circ_3-6s^3D_3$
1, 885. 28	2	53, 042	$4d^1D_2-5p^3D^\circ_2$
1, 867. 04	3	53, 560	$5p^1F^\circ_3-6s^1D_2$
1, 864. 06	20	53, 646	$4d^3F_2-5p^1P^\circ_1$
1, 853. 43	8	53, 954	$4d^1D_2-5p^3D^\circ_3$
1, 836. 13	0	54, 462	$5p^1D^\circ_2-6s^1D_2$
1, 831. 88	4	54, 588	$4d^3F_4-5p^3F^\circ_3$
1, 805. 33	30	55, 391	$4d^3F_3-5p^3F^\circ_3$
1, 800. 04	20	55, 554	$4d^3F_2-5p^3F^\circ_2$
1, 798. 16	30	55, 612	$4d^3F_2-5p^3D^\circ_1$
1, 793. 64	30	55, 752	$4d^3F_3-5p^3D^\circ_2$
1, 790. 24	30	55, 858	$4d^3F_4-5p^3D^\circ_3$
1, 783. 34	5	56, 074	$4d^3F_2-5p^3F^\circ_3$
1, 779. 55	30	56, 193	$4d^3F_4-5p^3F^\circ_4$
1, 771. 96	5	56, 434	$4d^3F_2-5p^3D^\circ_2$
1, 764. 80	1	56, 663	$4d^3F_3-5p^3D^\circ_3$
1, 754. 44	6	56, 998	$4d^3F_3-5p^3F^\circ_4$
1, 675. 81	0	59, 672	$4d^3F_3-5p^3P^\circ_2$
1, 675. 20	0	59, 694	$4d^3F_2-5p^3P^\circ_1$
871. 46	5	114, 749	$4d^3P_2-4f^3P^\circ_1$
869. 07	5	115, 065	$4d^3P_1-4f^3P^\circ_0$
868. 67	5	115, 118	$4d^3P_2-4f^3P^\circ_2$
867. 55	4	115, 267	$4d^3P_1-4f^3P^\circ_1$
865. 52	4	115, 537	$4d^3P_0-4f^3P^\circ_1$
864. 85	6	115, 626	$4d^3P_1-4f^3P^\circ_2$
859. 64	12	116, 327	$4d^3F_4-4f^3F^\circ_4$
853. 74	10	117, 131	$4d^3F_3-4f^3F^\circ_4$
841. 44	12	118, 843	$4d^3F_3-4f^3F^\circ_3$
836. 62	5	119, 528	$4d^3F_2-4f^3F^\circ_3$

TABLE 6.—*Classified lines of Zr III*—Continued

λ I. A.	Intensity and notes	ν	Term combinations
827. 93	12	120, 783	$4d^3F_3-4f^3F^\circ_2$
825. 67	3	121, 113	$4d^3F_4-4f^3G^\circ_4$
824. 19	3	121, 331	$4d^3F_3-4f^3G^\circ_3$
823. 60	20d	121, 418	$4d^3F_2-4f^3F^\circ_2$
822. 11	14	121, 516	$4d^3F_4-4f^3G^\circ_5$
820. 20	12	121, 921	$4d^3F_3-4f^3G^\circ_4$
819. 57	12	122, 015	$4d^3F_2-4f^3G^\circ_3$
812. 09	15	123, 139	$4d^1D_2-4f^1D^\circ_2$
809. 80	12	123, 487	$4d^1S_0-4f^1P^\circ_1$
806. 93	12	123, 926	$4d^1D_2-4f^1P^\circ_1$
784. 51	18	127, 468	$4d^1G_4-4f^1H^\circ_5$
779. 15	12	128, 344	$4d^1D_2-4f_1F^\circ_3$
775. 96	8	128, 872	$4d^1G_4-4f^1G^\circ_4$
773. 98	1	129, 202	$4d^1G_4-4f^1F^\circ_3$
765. 11	30	130, 700	$4d^3F_4-4f^3D^\circ_3$
764. 33	15	130, 833	$4d^3F_3-4f^3D^\circ_2$
763. 30	10	131, 010	$4d^3F_2-4f^3D^\circ_1$
760. 43	3	131, 504	$4d^3F_3-4f^3D^\circ_3$
756. 48	0	132, 191	$4d^3F_2-4f^3D^\circ_3$

TABLE 7.—*Triplet system multiplets from the transitions 5p→4d and 5p→5s*

	4d³F₂	4d³F₃ 682.5	4d³F₄ 804.3	4d³P₀	4d³P₁ 265.4	4d³P₂ 513.2	5s³D₁	5s³D₂ 403.9	5s³D₃ 730.7
5p³F°₄ 1,606.7		6 1,754.44 56,998	30 1,779.55 56,193						40 2,620.57 38,148.27
5p³F°₃ 519.8	5 1,783.34 56,074	30 1,805.33 55,391	4 1,831.88 54,588			4 2,116.32 47,236.82		20 2,682.18 37,272.05	20 2,735.79 36,541.72
5p³F°₂	20 1,800.04 55,554	4 {1,822.4 54,872}			4 2,116.63 47,229.90	3 2,139.86 46,717.25	20 2,690.51 37,156.66	7 2,720.08 36,752.75	5 2,775.26 36,022.05
5p³D°₃ 910.9	5 {1,743.8 57,346}	1 1,764.80 56,663	30 1,790.24 55,858			15 2,060.69 48,511.84		20 2,593.68 38,543.74	20 2,643.83 37,812.66
5p³D°₂ 822.2	5 1,771.96 56,434	30 1,793.64 55,752			12 2,077.83 48,111.73	2 2,100.28 47,597.52	20 2,628.28 38,036.36	20 2,656.48 37,632.62	18 2,709.06 36,902.25
5p³D°₁	30 1,798.16 55,612			10 2,102.27 47,552.47	6 2,114.07 47,287.08	3 9 {2,137.3 46,773.9}	20 2,686.30 37,214.89	18 2,715.76 36,811.22	
5p³P°₂ 658.9	{1,656.9 60,354}	0 1,675.81 59,672			20 1,922.02 52,028	40 1,941.15 51,515	4 2,382.60 41,958.14	12 2,405.78 41,553.91	40 2,448.86 40,822.96
5p³P°₁ −248.1	20 1,675.20 59,694			15 1,936.63 51,636	10 1,946.66 51,370	20 1,966.29 50,857	20 2,420.62 41,299.18	25 2,444.57 40,894.69	
5p³P°₀					15 1,937.29 51,618		10 2,406.18 41,547.00		
5p¹P°₁	20 1,864.06 53,646			{2,193.0 45,585}	{2,205.9 45,319}	{2,231.1 44,806}	10 2,836.19 35,248.22	12 2,869.06 34,844.42	

TABLE 8.—Multiplets from the transition 4f→4d

4d 4f	513.2 ³P₂	265.4 ³P₁	³P₀	804.3 ³F₄	682.5 ³F₃	³F₂
³G°₅				14 822.11 121,516		
³G°₄				3 825.67 121,113	12 820.20 121,921	12 819.57 122,015
³G°₃				{829.69 120,527}	3 824.19 121,331	
³F°₄				12 859.64 116,327	10 853.74 117,131	5 836.62 119,528
³F°₃				{847.18 118,039}	12 841.44 118,843	12? [1] 823.28 121,466
³F°₂					12 827.93 120,783	0 756.48 132,191
³D°₃				30 765.11 130,700	3 760.43 131,504	3 760.43 131,504
³D°₂					15 764.33 130,833	

³D°₁	10 763.30 131,010			
³P°₂			6 864.85 115,626	5 868.67 115,118
³P°₁		4 865.52 115,537	4 867.55 115,267	5 871.46 114,749
³P°₀			5 869.07 115,065	

¹ Calculated wave length. The observed line at 823.60 A is blended with another strong line.

TABLE 9.—*Multiplets from the transition 5d→5p*

	5p³F°₂	519.8 5p³F°₃	1,606.7 5p³F°₄	5p³D°₁	822.2 5p³D°₂	910.9 5p³D°₃	5p³P°₀	−248.1 5p³P°₁	658.9 5p³P°₂
5d³G₅ 1,112.4			8b 2,055.98 48,622.97						
5d³G₄ 556.2		6b 2,035.26 49,117.90	1b 2,104.26 47,507.51						
5d³G₃	4b 2,036.76 49,081.74	3b 2,058.57 48,561.80	1 2,129.12 46,952.87						
5d³F₄ 1,116.6		0 2,018.99 49,513.66	25 2,086.72 47,906.78						
5d³F₃ 632.1	1 2,043.61 48,917.24	8 2,065.60 48,396.55	{ 2,136.5 46,789.9 }						
5d³F₂	12 2,070.34 48,285.76	2 2,092.97 47,763.75							
5d³D₃ −31.3				{ 2,388.8 41,849.2 }	2d? 2,438.65 40,993.85	5 2,494.00 40,084.14			
5d³D₂					1 2,436.68 41,026.99	2 2,492.08 40,115.02		1 2,647.24 37,763.96	2 2,696.50 37,074.13
? 5d³D₁				(?)	(?)		(?)	(?)	{ 2,694.2 37,105.6 } (?)

	$5d\,^3P_2$ 784.5	$5d\,^3P_1$ −5.7	$5d\,^3P_0$
	3b 2,607.42 38,340.64	3 2,661.90 37,555.99	
	3 2,563.40 38,999.01	4 2,615.99 38,215.05	4 2,615.60 38,220.75
		1 2,633.09 37,966.89	

Inspection of Table 5 will reveal several pairs of terms which may be used for calculating series limits. These are shown to better advantage in Figure 4 in which terms of the same L value and of like parity are plotted on the same vertical line. Experience has shown that terms arising from the nd electrons are not satisfactorily represented by a simple Rydberg formula, which is theoretically accounted
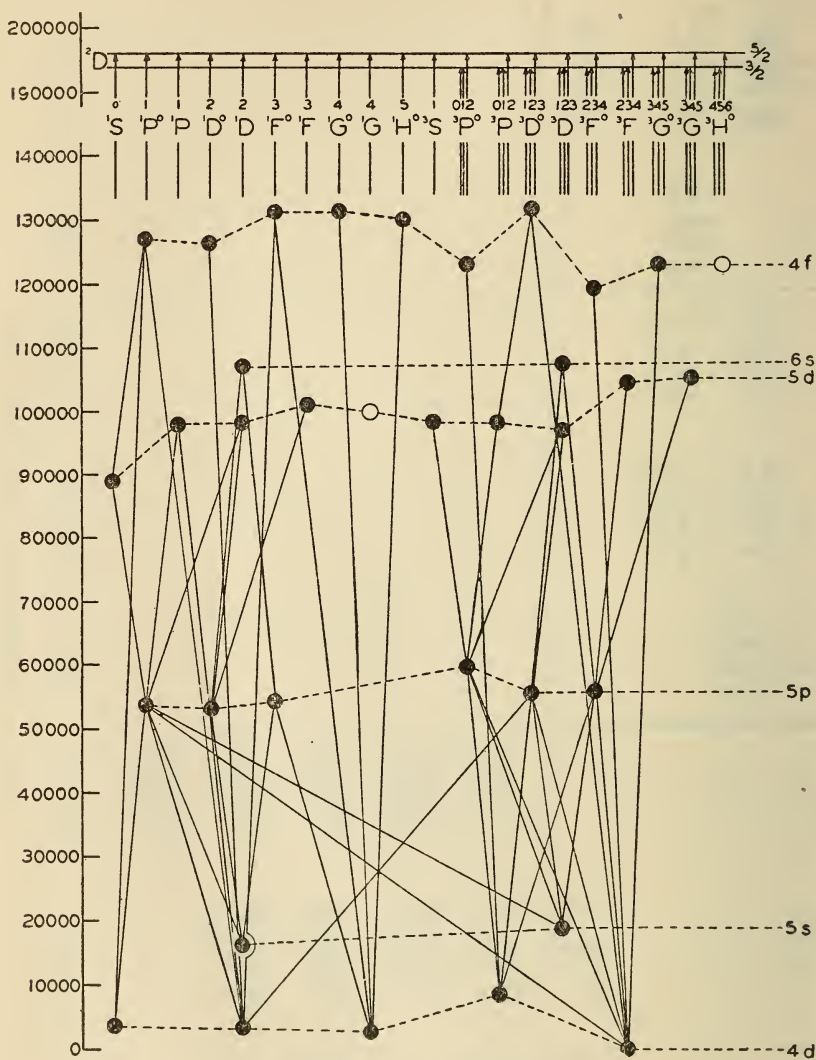

FIGURE 4.—*Term diagram of Zr III*

for by the strength with which the d electron of least n is bound in its orbit. That terms arising from configurations without s electrons tend to become more stable with increasing core charge was pointed out several years ago by Laporte [14] for the heavier atoms of the second long period. More recently Laporte and Lang [15] have demonstrated a similar property for the iso-electronic systems of Ni, Cu$^+$, and Zn^{++}.

[14] J. Opt. Soc. Am., **13**, p. 1; 1926.   [15] Phys. Rev., **30**, p. 378; 1928.

To establish the absolute term values of Zr III and to calculate the ionization potential of Zr^{++} we therefore make use of the sequences of ^1D and ^3D terms coming from the ns electrons. The manner in which the component series approach their limits in Zr IV is illustrated in the upper portion of Figure 4, which is taken from Hund.[16] The series of $^1D_2$ terms and those of $^3D_3$ terms both converge to $^2D_{5/2}$ of Zr IV, whereas the series of $^3D_2$ and $^3D_1$ both converge to $^2D_{3/2}$. In Table 10 we give the values for the series limits of Zr III as found by simple interpolation from Table III of Fowler's Report on Series in Line Spectra. The separation of the ground states of Zr III and Zr IV proves to be 194,441 cm^{-1}, which gives 24.00 v as the potential required to convert the doubly ionized Zr atom into the trebly ionized atom.

TABLE 10.—*Series limits of Zr III*

| Term sequence | Limiting term of Zr IV | | $^3F_2$—$^2D_{3/2}$ |
	$^2D_{3/2}$	$^2D_{5/2}$	
ns $\begin{cases}^1D_2 \\ ^3D_3 \\ ^3D_2 \\ ^3D_1\end{cases}$	194, 824 194, 268	195, 978 195, 195	194, 728 193, 945 194, 824 194, 268
Means	194, 546	195, 586	194, 441

$^2D_{5/2}$—$^2D_{3/2}$ $\begin{cases}\text{observed: } 1,250 \text{ cm}^{-1} \\ \text{calculated: } 1,040 \text{ cm}^{-1}\end{cases}$
I. P. $= 1,2345 \times 194,441 \times 10^{-4} = 24.00$ v.

In comparing the corresponding terms of Rb I, Sr II, Yt III, and Zr IV by means of the irregular doublet law it was noted above that the increase in value of the term 4^2D is anomalous. Therefore it becomes of interest to see to what extent the law holds for the spectra Sr I, Yt II, and Zr III, of the second long period, in view of the fact that Russell and Lang, in the work cited above, have shown its validity for the spectra Ca I, Sc II, and Ti III, of the first long period. That we may expect it to hold, at least approximately, for some of the terms is evident from the work of Gibbs and White, already referred to, who were able to detect with its aid the triplet system multiplets representing the electron transition $4d5p \rightarrow 4d5s$ both for Zr III and Cb IV.

Table 11 presents a comparison of the values of $\sqrt{\nu/R}$ calculated for corresponding terms of neutral Sr, singly ionized Yt, and doubly ionized Zr. The data for Sr I were taken from the analysis given by Russell and Saunders.[17] For Yt II the data were taken from the analysis given by Meggers and Russell.[18] The differences between the values of $\sqrt{\nu/R}$ for the terms belonging to the same configuration do not run as smoothly as previous comparisons of the kind for other atomic systems would indicate. The criticism may be raised at once

[16] Linienspektren und periodisches System der Elemente, p. 198; 1927. Julius Springer, Berlin.
[17] Astrophys. J., **61,** p. 38; 1925.
[18] B. S. Jour. Research, **2,** p. 733; 1929.

that some of the terms may not be correctly identified. The possibility of this, especially for singlet terms, is recognized. Thus, the difference 0.346 for the term $^1F^\circ_3$ of the $5p$ configuration appears to be too high. On this term depends the position of $4d^1G_4$, whose difference 0.445 also seems too high when compared with the difference 0.415 given by the well-established $^3P_2$ and $^3F_4$ terms of the $4d^2$ configuration. But if we compute the hypothetical positions of $4d^1G$, and also $4d^1D$, by assuming the difference 0.415 to hold for them as for the triplet terms, we get terms which require strong lines in regions of the spectrum where there are none and leave unclassified the strong lines which have been accounted for on the basis of the terms of Table 5. The term $4d^1D$, whose difference 0.438 appears too high in comparison with the 0.415 of the ^3P and ^3F terms, is, however, well-established through intersystem combinations.

TABLE 11.—*Comparison of Sr I, Yt II, and Zr III*

Electron configuration	Term	$\sqrt{\nu/R}$				
		Sr I	Δ	Yt II	Δ	Zr III
4d.4d	$^3F_4$			0. 917	0. 414	1. 331
	$^3P_2$	0. 382	0. 508	. 890	. 415	1. 305
	$^1G_4$			. 882	. 445	1. 327
	$^1D_2$			. 886	. 438	1. 324
	$^1S_0$					1. 323
4d.5s	$^3D_3$	. 622	. 331	. 953	. 311	1. 264
	$^1D_2$	. 609	. 335	. 944	. 331	1. 275
4d.5p	$^3F^\circ_4$	. 495	. 323	. 818	. 304	1. 122
	$^3D^\circ_3$	. 470	. 343	. 813	. 310	1. 123
	$^3P^\circ_2$	. 462	. 334	. 796	. 315	1. 111
	$^1F^\circ_3$			. 790	. 346	1. 136
	$^1D^\circ_2$			. 830	. 310	1. 140
	$^1P^\circ_1$			. 823	. 315	1. 138
4d.5d	$^3G_5$			. 618	. 285	. 903
	$^3F_4$			. 602	. 304	. 906
	$^3D_3$			. 622	. 325	. 947
	$^3P_2$			. 582	. 358	. 940
	$^3S_1$			. 608	. 351	. 959
	$^1G_4$			. 592		
	$^1F_3$			. 628	. 299	. 927
	$^1D_2$			. 613	. 331	. 944
	$^1P_1$			. 619	. 325	. 944
	$^1S_0$			. 620	. 366	. 986
4d.6s	$^3D_3$			. 648	. 245	. 893
	$^1D_2$			. 648	. 248	. 896

Among the triplet terms of the $5d$ group the differences between the $\sqrt{\nu/R}$ of Yt II and Zr III range from 0.285 to 0.358. The reality of the terms is, however, well attested by the multiplets resulting from their combination with the triplet terms of the $5p$ electron, which give well-established satellite separations. It is not surprising, therefore, that the singlet terms of the same configuration exhibit the same range in the differences between the $\sqrt{\nu/R}$ values. It thus seems highly probable that the spectral terms of the heavier atomic systems conform only approximately to the irregular doublet law.

V. COMPARISON WITH Ti IV AND Ti III

The main features of the analysis of Zr IV and Zr III presented in this paper closely resemble those found for Ti IV and Ti III by Russell and Lang.[19] But there are some differences between the spectra of the two elements deserving remark. The Zr multiplets are all of longer wave length than their Ti counterparts, owing to the contraction of the Zr term structure as compared with that of Ti. This fact is responsible for bringing into the domain of observation the $4f$ multiplets of Zr III which are missing from Ti III and for placing beyond observation the 5D-4F combination of Zr IV which has been observed for Ti IV. In Zr III the metastable singlet terms of the $4d^2$ configuration all lie close together with ^1G lowest, whereas in Ti III both ^1S and ^1G are approximately 6,000 cm^{-1} above ^1D. Of the Zr III terms, ^1D and ^3D, coming from the $5s$ electron, the singlet term is the lower; in Ti III the triplet term lies lower. This characteristic of the Zr III terms is, however, confirmed by the analysis of Zr II (to be presented in a subsequent paper in this Journal). Each of them serves as the limit of series of doublet P, D, and F terms of Zr II obtained by adding p electrons to the $4d\ 5s$ configuration. Two triads coming from $4d\ 5s\ 5p$ have been found in Zr II, separated by approximately 10,000 cm^{-1}. In the lower triad the component terms are separated by small $\Delta\nu$'s, indicating their origin in a singlet term, whereas in the higher triad the $\Delta\nu$'s are large, which indicates their origin in the triplet term.

A further point of difference between Zr III and Ti III is in the character of the intersystem combinations. In Ti III the observed lines of this class are all faint; in Zr III they are strong. According to Kronig's [20] extension of Sommerfeld's qualitative intensity rule those term combinations are most intense for which the change, ΔL, in the quantum numbers of the terms is the same as the change, Δk, in the azimuthal quantum number of the series electron. Two of the intersystem multiplets of Zr III represent combinations which should be weak or missing according to this rule, and combinations which we might expect to occur, and do occur faintly in Ti III, are missing from Zr III.

This departure from the intensity rule is apparent also among the $4f \rightarrow 4d$ multiplets, Table 8. Here the combination $^3D° \rightarrow {}^3F$ is clearly stronger than the $^3G° \rightarrow {}^3F$ combination, and $^3P° \rightarrow {}^3P$ is present with moderate intensity, whereas the expected $^3D° \rightarrow {}^3P$ multiplet is missing. Unfortunately the corresponding multiplets of Ti III are not available for comparison. The tendency to deviate from the rule is likewise shown by the Zr III multiplets representing the transitions $5p \rightarrow 4d$ and $5d \rightarrow 5p$, Tables 7 and 9. The strongest groups are those for which $\Delta L = 0$, although the multiplets for which $\Delta L = \pm 1$ are also prominent in the $5p \rightarrow 4d$ group but much weaker or missing in the $5d \rightarrow 5p$ group. The same effect is noticeable among the corresponding Ti III multiplets. The $5p \rightarrow 5s$ multiplets of Zr III, Table 7, show no marked differences in intensity, whereas in Ti III they conform strictly to the above rule.

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[19] Astrophys. J., **66**, p. 13; 1927.　　　[20] Zeit. für Physik, **33**, p. 261; 1925.

VI. CONCLUSION AND ACKNOWLEDGMENTS

The classified lines of Zr IV and Zr III can all be accounted for by means of the terms required theoretically for atomic systems with one and two external electrons. When these lines are stricken from the lists of observed wave lengths there still remain many, mostly faint, of unknown origin. Some may be due to impurities, but it is more probable that the majority of these unclassified lines result from excitation of the outermost electrons of the krypton configuration.

Washington, April 3, 1930,